

# A Study of the Uptake and Gelation Reactions of Cr(III) Oligomers with Polyacrylamide

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**ABSTRACT:** The reaction rates of Cr(III) oligomers with partially hydrolyzed (PAAm) polyacrylamide were measured. The oligomers were prepared in relatively pure form using liquid chromatography, allowed to react with polymer, quenched, and then separated using equilibrium dialysis. In the pH range of 4–5, Cr(III) concentrations in the range of 8–30 ppm and polymer concentrations in the range of 4000–20,000 ppm, reaction rates increased with increasing oligomer size, concentration, and pH. Gelation rates determined using rheological measurements were found to follow closely the Cr(III) reaction rates. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1381–1391, 1997

## INTRODUCTION

Cr(III) solutions are commonly used with dilute solutions of polymers with carboxyl side chains to form *in situ* gels in heterogeneous and/or fractured oil reservoirs where they divert displacement fluids from high permeability to lower permeability reservoir zones. A typical gelling solution preparation technique is addition of a monomeric Cr(III) salt solution to a polymer solution. Until recently, it was generally assumed that the Cr(III) remained in monomeric form during the gelation.<sup>1,2</sup> The results of recent studies, however, indicate that under typical gelation conditions, Cr(III) also reacts with itself to form higher molecular weight Cr(III) oligomers [Cr(III) oligomerization].<sup>3,4</sup>

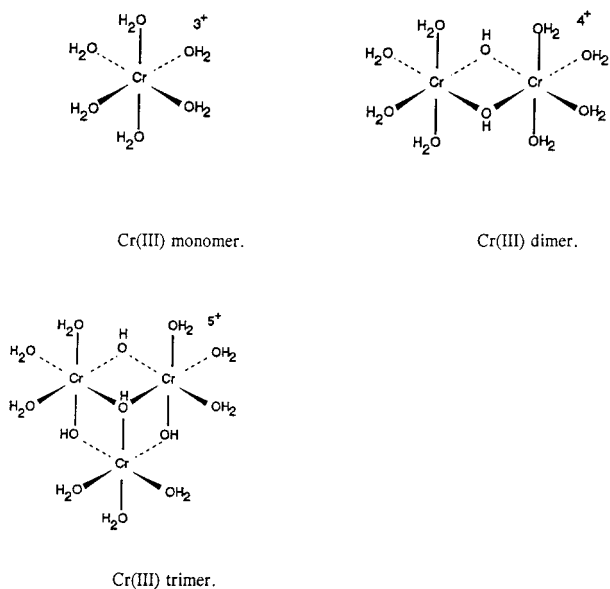
The Cr(III) oligomers potentially present in Cr(III)–polymer gelling solutions have different gelation characteristics. The rates of gelation increase with increasing oligomer size, with the ge-

lation times for the higher molecular weight oligomers being particularly rapid.<sup>5,6</sup> The pH ranges over which gelation occurs also increase as the size of the oligomer increases.<sup>7</sup> The amounts of total Cr(III) necessary for gelation generally decrease as the oligomer size increases.<sup>6</sup>

The broader ranges of gelation times and usable gelling solution pH values obtained from using the different-sized Cr(III) oligomers indicate the possibility of using mixtures of Cr(III) oligomers to perform permeability modification treatments over wider ranges of field conditions than those currently possible with the commonly used monomeric Cr(III)–polymer systems. The lower Cr(III) concentrations necessary for gelation with the Cr(III) dimer and trimer<sup>6</sup> indicate that significantly lower levels of total Cr(III) are possible if higher molecular weight oligomer solutions are used instead of Cr(III) monomeric salt solutions. However, in order to utilize the different Cr(III) oligomers in permeability modification treatments, more quantitative information on the reactions of the oligomers with carboxyl-containing polymers is necessary. In this study, the reactions

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**Figure 1** Cr(III) oligomers.

of Cr(III) monomer, dimer, and trimer (Fig. 1) with partially hydrolyzed polyacrylamide (PAAm) were followed to assess the effects of oligomer type, pH, oligomer concentration, and PAAm concentration on the reactions of Cr(III) oligomers with PAAm. Rates of gelation of the solutions were also monitored with rheological measurements on the reacting systems.

## EXPERIMENTAL SYSTEM

### Experimental Conditions

Two types of experiments were performed. The first consisted of experiments that followed the reaction of free solution Cr(III) with PAAm (termed here the uptake reaction) in gelling solutions prepared from essentially pure monomer, dimer, or trimer oligomer solutions. The second type consisted of rheological measurements that followed the relative rates of gelation of solutions of the same concentrations as those used in the uptake reaction experiments.

Two sets of experimental conditions were used to characterize the uptake and gelation processes. The first set used 25 ppm Cr(III), PAAm concentrations between 4400 and 19,800 ppm, 1M NaClO<sub>4</sub>, and an initial gelling solution pH value of 4. The second set used 10 ppm Cr(III), 15,000 ppm PAAm, 1M NaClO<sub>4</sub>, and an initial solution pH of 5. For both systems, 0.01M NaOH was used to adjust the pH and a base temperature of 25°C

was maintained. These experimental conditions were chosen because they resulted in H<sup>+</sup> and PAAmcarboxyl concentrations which remained approximately constant during the experiments, allowed for adequate mixing of the gelling solutions, produced reasonable gelation times, and allowed relatively good accuracy in the Cr(III) concentration measurements.<sup>8</sup>

### Preparation and Characterization of the Cr(III) Purified Oligomer Solutions

Stock solutions of chromic perchlorate were prepared by reducing CrO<sub>3</sub> with 30% H<sub>2</sub>O<sub>2</sub> in the presence of an excess of perchloric acid, followed by neutralization to pH 3 with NaHCO<sub>3</sub>. Chromium(II) perchlorate was prepared by passing the chromic perchlorate stock solution through zinc amalgam in a Jones reductor. The Cr(II) solution was oxidized to a mixture of monomer, dimer, trimer, and higher Cr(III) oligomers by bubbling vigorously with O<sub>2</sub> gas for 30 min.

The multioligomer solution was adsorbed onto a Sephadex C-25 ion exchange column. The Cr(III) monomer, dimer, and trimer were successively eluted by solutions of sodium perchlorate of increasing salt concentration and decreasing pH with the purple monomer being eluted first, the blue-green dimer second, and the green trimer third. The oligomer solutions were collected off the early portions of each color band to minimize the concentrations of higher molecular weight oligomers in each purified solution.

The monomer, dimer, and trimer were identified from their UV absorption spectra.<sup>9,10</sup> The Cr(III) concentrations of the oligomer solutions were determined by oxidation of the Cr(III) to Cr(VI) with excess 30% H<sub>2</sub>O<sub>2</sub> under alkaline (pH 11–12) conditions and measurement of the UV absorbance at 374 nm.<sup>8</sup> NaClO<sub>4</sub> concentrations were determined from the oligomer solution densities and a standard curve of density versus NaClO<sub>4</sub> concentration.<sup>8</sup>

The oligomer solution purities were established by oligomer separation on an analytical liquid chromatography (HPLC) column, followed by conversion of the HPLC oligomer peak heights to oligomer concentrations. A Wescan cation-exchange column (Cat. No. 269–004) and a Wescan Cation guard column (Cat. No. 269081) in series with a Waters Chromatograph pump (Model 6000A), an in-line Waters 490 Programmable Multiwavelength UV detector (3 mm path length and 2.7 μL volume), and a Cole–Parmer chart

recorder (Model No. 8373–20) were used with a Rheodyne 100  $\mu\text{L}$  injection loop (Model 7125). The oligomers were separated using 0.4M  $\text{Mg}(\text{NO}_3)_2$  eluant solution adjusted to pH 2.5 with 6 N  $\text{HNO}_3$ . The monomer and dimer solutions were separated at an eluant flow rate of 1 mL/min. The trimer was separated from the monomer and dimer at a flow rate of 2 mL/min. The oligomer HPLC peak heights at the wavelengths characteristic of each species (monomer; 408, 576 nm; dimer; 418, 582 nm, trimer: 426, 584 nm<sup>8</sup>) were measured at their characteristic HPLC elution times and converted to oligomer concentrations through standard curves. Higher oligomers were not present in concentrations that could be detected in the purified monomer solutions. The dimer solution contained less than 5% monomer and no detectable trimer. The trimer solutions contained less than 5% monomer and/or dimer. Stock oligomer solution concentrations were determined by conversion of the Cr(III) to Cr(VI) with  $\text{H}_2\text{O}_2$  and base, followed by measurement of the UV absorbances at 374 nm.<sup>8</sup>

#### Preparation and Characterization of the PAAm Solutions

The polymer used was a 2.3% partially hydrolyzed polyacrylamide. Stock PAAm solutions with nominal concentrations of 20,000–30,000 ppm were prepared from Aldrich PAAm (cat. 18,127–7. Lot 9; nominal MW 5–6,000,000). The PAAm was added to 1M  $\text{NaClO}_4$  brine solutions, stirred for 3 days, and allowed to set for at least 5 days before use in preparation of the gelling solutions. The solutions were stored at 4°C between runs, with the PAAm solutions for each experiment being placed in a 25°C water bath 12 h before runs.

The PAAm amide UV absorbances were measured at 236 nm and converted to PAAm concentrations through standard curves of UV absorbance vs. PAAm concentration, constructed using purified PAAm solutions.<sup>8</sup> PAAm/carboxyl concentrations were obtained by multiplying the PAAm concentrations by 0.023, the fraction of the PAAm side groups that were carboxyl groups.<sup>11</sup>

#### Measurement of the Rate of Cr(III) Oligomer Uptake by PAAm

The method for determining rate of uptake consisted of first mixing a measured amount of Cr(III) oligomer with a known concentration PAAm solution. The mixture was allowed to react

at a temperature of 25°C. At specified times, a sample was removed, quenched, and placed in a dialysis cell where free Cr(III) oligomer moved across the dialysis membrane and equilibrated. Measurement of the Cr(III) concentration on both sides of the cell, after equilibration, allowed calculation of the amount of Cr(III) that had reacted with the PAAm.

During the reaction phase, the pH of the solution was held constant through the addition of 0.01M NaOH using an automatic titrator. The titrator system consisted of a Fisher Model 380 titrator with a Fisher pH and reference electrode pair, a Fisher Model 383 AEP Demand Module, and a Fisher Model 395 Burrett Dispenser. An outer reference electrode fill solution of 1M  $\text{Na}_2\text{SO}_4$  was used instead of the saturated KCl solution supplied with the electrode to avoid the formation and precipitation of  $\text{KClO}_4$  on the reference electrode junction. Temperature was kept constant at 25°C with a circulating, constant-temperature water bath.

Samples were removed periodically and the Cr(III)–PAAm reactions were quenched by diluting the samples in 1 : 10 or 1 : 20 gel/brine ratios with 1M  $\text{NaClO}_4$  brine. Five milliliters of the diluted gel sample were placed on the retentate side of a dialysis cell, and 5 mL of 1M  $\text{NaClO}_4$  brine at the gelling solution pH were placed on the diffusate side of the dialysis cell. A 0.05 micron Micropore polycarbonate filter separated the retentate and diffusate chambers and allowed free movement of the unreacted oligomers and solvent while preventing the movement of the PAAm and the Cr(III) attached to the PAAm.<sup>8</sup> The dialysis cells consisted of circular, Teflon discs with a inner dialysis volume of approximately 7 cm<sup>3</sup>.<sup>1</sup> The filled dialysis cells were continuously rotated in a 25°C water bath for 3 h, during which time equilibrium of the free-solution oligomers between the retentate and diffusate chambers was obtained.<sup>8</sup>

After removal of the retentate and diffusate solutions from the dialysis cells, excess NaOH and  $\text{H}_2\text{O}_2$  were added to convert the Cr(III) to Cr(VI) and the PAAm to gaseous byproducts.<sup>8</sup> After 4–8 days, the Cr(VI) concentrations of the retentate and diffusate solutions were measured at 374 nm on a Perkins–Elmer Lambda 3 UV spectrophotometer. Samples were degassed in a sonic mixer for approximately 5 min before readings were taken. Cr(VI) concentrations were determined from the UV absorbances and a standard Cr(VI) vs UV absorbance curve. Experiments performed on gels prepared with standard Cr(III) solutions

indicated that measured Cr(VI) concentrations were within 6% of the true concentrations. The measured Cr(VI) concentrations on the diffusate side of the cells represented free Cr(III). It was assumed that the free Cr(III) concentration on the retentate side was the same as the measured value on the diffusate side. Because volumes were equal on the two sides of the cell, fractional free Cr(III) concentrations were determined by dividing twice the diffusate concentration by the sum of the measured diffusate and retentate concentrations.

### Monitoring of Gelation Rates Using Rheological Measurements

Immediately after preparation of a gelling solution, a volume of 29 mL was placed in a Bohlin Rheologi-controlled stress rheometer using a double-gap geometry. The temperature was maintained at 25°C through a Neslab Instruments Inc. temperature control unit designed specifically for use with the Bohlin Rheologi rheometer and controlled through a Bohlin CS rheometer interface. A 29 cp standard oil was applied to the exposed outer and inner fill surfaces of the gelling solution to prevent evaporation. The gelling solution was submitted to intermittent oscillation (5 s/180 s) at a frequency of 1 Hz, with rheological measurements being taken every 3 min. The oscillatory stress was held constant, with the oscillatory strain (initially 0.28) decreasing as the gelations proceeded. The gelling solution rheological data were collected and converted to storage moduli ( $G'$ ) and loss moduli ( $G''$ ) values using software provided by Bohlin with a Compaq DESKPRO 386/20e personal computer connected to the Bohlin CS rheometer interface.

### Cr(III)–PAAm UPTAKE REACTION: RESULTS AND DISCUSSION

The effects of oligomer type, PAAm concentration, and gelling solution pH on the rates of monomer, dimer, and trimer uptake by PAAm were explored. Three sets of runs were performed for each of the oligomer types and PAAm concentrations used. Run conditions are summarized in Table I. Representative data are shown in Figures 2–5 where the ratio of free Cr(III) to total Cr(III) in the system is plotted as a function of time.

### Effect of Oligomer Type on the Oligomer–PAAm Uptake Rates

Representative data showing the effect of oligomer type on the rate of oligomer uptake by PAAm are shown in Figures 2–3. For the comparisons presented in each figure, pH, overall Cr(III) concentration, and PAAm concentration were approximately the same. The essential difference was oligomer type. The results showed that the uptake rate was fastest for the trimer and slowest for the monomer at pH values of both 4 and 5.

Additional comparisons are shown in Table II, where amounts of monomer, dimer, and trimer reacting with PAAm at 3 h (pH 4) and 1 h (pH 5) are summarized for several runs. Separate oligomerization experiments<sup>8</sup> indicated that, for these reaction times, less than 6% of the original oligomers had formed higher molecular weight oligomers. Therefore, the amounts of oligomer uptake in Table II are representative of the monomer, dimer, and trimer uptake reactivity with the PAAm. For longer reaction times, interpretation of the results in terms of individual oligomer reactivities is less definitive because the potential for significant amounts of higher molecular weight oligomer products increases with reaction time.<sup>3</sup>

The results in Table II also show that the uptake rates are fastest for the trimer and slowest for the monomer. The rates of dimer and trimer reaction are greater than those expected from assuming equal molar rates of reaction, suggesting that dimer and trimer are more reactive on a molecular level with the PAAm than the monomer, with the trimer particularly exhibiting high reactivity with the PAAm.

### Effect of PAAm Concentration on the Oligomer–PAAm Uptake Rates

The effect of PAAm concentration on oligomer–PAAm uptake rate was examined by performing a series of runs for each oligomer. In each series, pH was initially set at 4 and Cr(III) concentrations were approximately equal, but three different PAAm concentrations were used. Data for the three trimer runs are given in Figure 4 and the data for all the PAAm concentration comparison runs are listed in Table II. The increase in uptake rate with PAAm concentration is consistent with the trends found by Hunt<sup>1</sup> and Lockhart,<sup>12</sup> who investigated the reaction of Cr(III) monomeric salt solutions with PAAm.

**Table I Summary of the Experimental Conditions for the Uptake Runs**

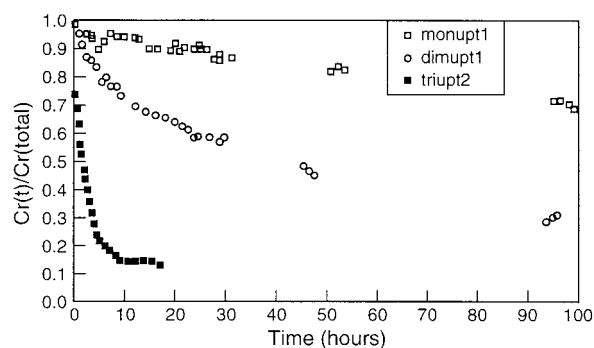
Run No. <sup>a</sup>	[Cr(III)] (ppm)	[Cr(III)] (mM) <sup>b</sup>	[PAAm] (ppm)	Average pH
monupt1	27.3	0.558	8,782	3.97
monupt2	25.4	0.519	13,441	4.06
monupt3	30.6	0.625	14,857	3.98
monupt4	27.3	0.558	19,908	4.02
monupt5	10.9	0.225	15,000	4.99
dimupt1	25.3	0.258	8,427	3.95
dimupt2	24.3	0.248	14,415	3.96
dimupt3	17.3	0.177	19,274	3.97
dimupt4	8.3	0.085	15,050	5.05
triupt1	24.7	0.168	4,433	3.90
triupt2	24.1	0.164	8,633	3.92
triupt3	22.8	0.155	13,153	3.93
triupt4	19	0.130	14,667	3.94
triupt5	7.4	0.050	14,657	3.95
triupt6	7.6	0.051	14,923	3.94
triupt7	10.8	0.074	14,045	4.98

<sup>a</sup> Monomer, dimer, and trimer runs are designated by mon, dim, and tri, respectively.

<sup>b</sup> Concentrations are in mM oligomer.

### Effect of Gelling Solution pH on the Oligomer–PAAm Uptake Rates

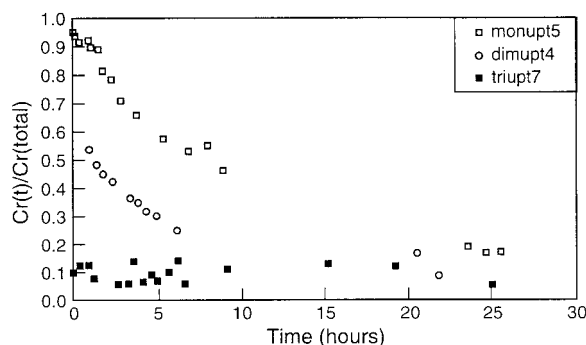
The effect of solution pH was studied by comparing trimer uptake runs, at comparable oligomer and PAAm concentrations, at pH 4 and 5. The results given in Figure 5 and Table II indicate that uptake rates increase with increasing pH. The trimer–PAAm uptake is particularly rapid at pH 5, where 90% of the trimer had reacted with the PAAm by the time the first sample was taken, approximately 5 min after the start of the addition of the stock trimer solution to the PAAm solution. Runs triupt 5 and triupt 6 in Figure 5 are at comparable conditions and indicate the level of reproducibility.



**Figure 2** The effect of oligomer type on the fractional uptake at pH 4 using 24.1–27.3 ppm Cr(III) and 8427–8782 ppm PAAm (monupt1, dimupt1, triupt3, Table I).

### GELATION RESULTS AND DISCUSSION

The effects of oligomer type, concentration, and solution pH on gelation rate were examined by following the storage ( $G'$ ) and loss ( $G''$ ) moduli as functions of time. Two relative measures of the rates of gelation were used that are based on rheological measurements. The first was the initial slope of the curve of storage modulus ( $G'$ ) vs. time.<sup>2,13,14</sup> As discussed in the uptake section, insignificant amounts of higher molecular weight oligomers were present during the initial experimental time periods. The initial slopes of  $G'$  vs. time were then relative measures of the rate of



**Figure 3** The effect of oligomer type on the fractional uptake at pH 5 using 8.3–10.9 ppm Cr(III) and 14,045–15,050 ppm PAAm (monupt5, dimupt4, triupt7, Table I).

**Table II Comparison of Amounts of Oligomers Reacted with PAAm at Early Times**

[PAAm] (ppm)	pH	[Cr(III)] (ppm)	Uptake Reaction Time (h)	% Monomer Reacted	% Dimer Reacted	% Trimer Reacted
4433	4	24.7	3			57
8427–8782	4	24.1–25.3	3	6	15	65
13,153–14,415	4	22.8–25.4	3	7	20	78
19,274–19,908	4	17.3–27.3	3	8	30	
15,000–15,050	5	8.3–10.9	1	10	47	87
14,657–14,923	4	7.4–7.6	1			52

gelation for the monomer, dimer, and trimer solutions. In the second method, gelation time was defined as the time where the  $G'$  value had increased to the value of the loss modulus ( $G''$ ).<sup>12,15,16</sup> It was assumed that at this condition the gelling solution solid or elastic properties, as represented by the  $G'$  value, were equal to the liquid or viscous properties, as represented by  $G''$ .<sup>16</sup> Because of the sensitivity of the initial  $G'$  values to PAAm concentrations, the increases in  $G'$  values above the zero-time  $G'$  values were used for the direct graphical comparisons.

#### Effect of Oligomer Type on the Rate of Gelation

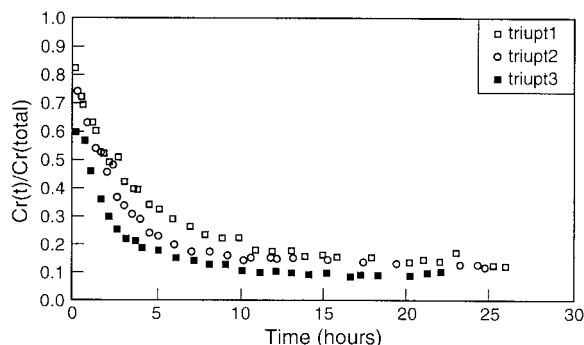
The effect of oligomer type on the rate of gelation was examined for three sets of conditions for pH, and Cr(III) and PAAm concentrations. Representative  $G'$ -vs.-time data for one set of conditions are shown in Figure 6, with gelation parameters for all systems listed in Table III.  $G'$  values increased with time and often did not reach a maximum during the time of the experiment.  $G'$  values at the time when  $G'$  became equal to  $G''$  were

significantly less than the final  $G'$  achieved during the experiment.

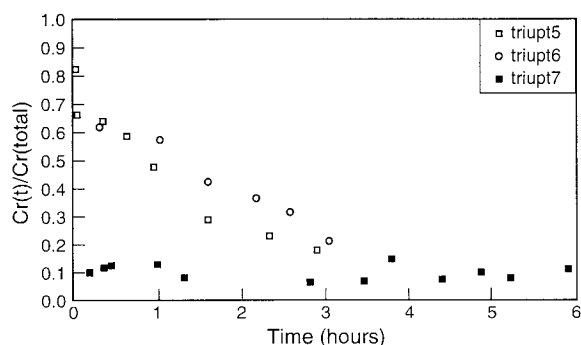
The initial slopes of  $G'$  vs. time and  $G'-G''$  crossing times shown in Table III indicate that at comparable total Cr(III) concentrations (similar ppm), the rates of gelation are slowest with the monomer, more rapid with the dimer, and significantly faster with the trimer. The increase in gelation rate with increasing oligomer size is even more apparent when molar oligomer concentrations are compared. Because the trimer and dimer molar concentrations are  $\frac{1}{3}$  and  $\frac{1}{2}$  of the monomer concentrations, the large trimer  $G'$  slopes indicate that the trimer was as much as 100 times more reactive on a molecular basis than the dimer or monomer. The rapid rates of gelation that occur with the trimer confirm the qualitative results of Fei and Mertes,<sup>6</sup> who found spontaneous gelation upon mixing trimer with PAAm solutions in systems using 80 ppm trimer, 5000 ppm PAAm, and a gelling solution pH of 4.5.

#### Effect of Oligomer Concentration on the Gelation Rate

The effect of oligomer concentration on gelation rate was examined by running gelation experi-



**Figure 4** The effect of PAAm concentration on the fractional uptake of trimer at pH 4 using 22.8–24.7 ppm Cr(III) and 4433 ppm (triupt1), 8,633 ppm (triupt2), and 13,153 ppm (triupt3) PAAm (Table I).



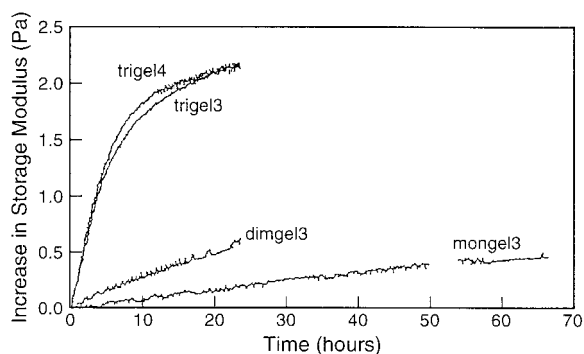
**Figure 5** The effect of pH on the fractional uptake of trimer using 7.1–10.8 ppm Cr(III), 14,045–14,923 ppm PAAm, and pH values of 4 (triupt5 and triupt6) and 5 (triupt7) (Table I).

**Table III Comparison of the Initial  $G'$  vs. Time Slopes and the  $G'-G''$  Crossing Times for the Oligomer-PAAm Gelation Runs**

Gelation Run	pH	[Cr(III)] (ppm)	[Cr(III)] (mM) <sup>a</sup>	[PAAm] (ppm)	Initial Slope (Pa/h)	$G'-G''$ Crossing Time (h)
mongel1	4	21.9	0.447	15,309	0.0255	47
mongel2	4	24.6	0.502	15,462	0.0313	no crossing up to 24 h
dimgel1	4	21	0.215	14,766	0.0631	25
dimgel2	4	21	0.215	14,828	0.0644	no crossing up to 14 h
trigel1	4	19	0.129	14,666	0.951	1.6
trigel2	4	21	0.143	14,980	1.10	1.9
mongel3	4	11.7	0.238	14,965	0.0080	no crossing, up to 67 h
dimgel3	4	10.9	0.111	14,980	0.024	no crossing up to 25 h
trigel3	4	7.4	0.050	14,715	0.295	11.3
trigel4	4	7.6	0.051	14,963	0.299	8.4
mongel4	5	10.9	0.225	15,000	0.19	15
dimgel4	5	8.3	0.085	15,050	0.19	24.3
trigel5	5	10.8	0.074	14,045	1.10	2.6

<sup>a</sup> Cr(III) concentrations are in mM oligomer.

ments for each oligomer at two different Cr(III) concentrations. For comparison purposes, the  $G'$  slope and  $G'-G''$  crossing times from the replicate runs at the higher Cr(III) concentrations were each averaged and then compared against the values from the runs at the lower Cr(III) concentration in Table IV. For each oligomer, the initial slopes of the  $G'$  vs. time curves are higher for the higher oligomer concentration. The slope ratios are 30–80% higher than the oligomer molar ratios, indicating that the relative gelation rates increase above that expected from a linear dependence of gelation rate on oligomer concentration. Representative data for the dimer runs are shown in Figure 7.



**Figure 6** The effect of oligomer type on the increase in  $G'$  for the gelation runs at pH 4 using 7.4–11.7 ppm Cr(III) and 14,657–14,965 ppm PAAm (mongel3, dimgel3, trigel3, trigel4, Table III).

### Effect of pH on the Gelation Rate

The effect of pH on the rate of gelation was examined by performing gelation experiments with each oligomer type at gelling solution pH values of 4 and 5. The monomer comparative runs are shown in Figure 8, with the  $G'$  slopes and  $G'-G''$  crossing times from the complete set of runs listed in Table V. With each oligomer, the slopes of the plots of  $G'$  vs. time increase with pH, with the largest increase (2400%) occurring between the monomer solutions and the smallest increase (370%) occurring between the trimer solutions.

### COMPARISON OF THE RELATIVE RATES OF UPTAKE AND GELATION

Six of the uptake and gelation runs were performed at comparable oligomer type, pH, and Cr(III) and PAAm concentrations.<sup>8</sup> This allowed the comparison of the relative rates of uptake and gelation through crossplotting the fractional Cr(III) reacted with the PAAm against the increase in  $G'$  with time.

During the initial time periods for all the monomer, dimer, and trimer runs, the increases in  $G'$  approximately paralleled the increases in the oligomer-PAAm uptake,<sup>8</sup> as illustrated in Figures 9–11. In these figures, increases in storage modulus and relative amount of chromium reacted are plotted vs. time. For the pH 4 and pH 5 monomer and dimer runs, the increases in  $G'$

**Table IV** Effect of Oligomer Concentration on the Rates of Gelation

Gelation Run(s)	Average [Cr(III)] (ppm)	Ratio, [Cr] <sub>1</sub> /[Cr] <sub>2</sub> <sup>a</sup>	Average Initial Slope (Pa/h)	Ratio, Slope <sub>1</sub> /Slope <sub>2</sub> <sup>a</sup>	G'–G'' Crossing Time (h)
mongel1 and mongel2	23.3	2.0	0.0285	3.56	47
mongel3	11.7		0.008		no crossing
dimgel1 and dimgel2	21	1.91	0.0638	2.66	25
dimgel3	10.9		0.024		no crossing
trigel1 and trigel2	20	2.67	1.02	3.43	1.7
trigel3 and trigel4	7.5		0.297		10.6

<sup>a</sup> [Cr]<sub>1</sub> is the higher Cr(III) concentration, [Cr]<sub>2</sub> is the lower concentration.

and uptake increased in parallel for most of the experimental time periods, whereas the  $G'$  values in the trimer runs continued to slowly increase after most of the trimer uptake had occurred. This indicates that the uptake and gelation reactions generally occurred over the same time frame, with the delayed gelation reactions in the trimer runs possibly resulting from higher molecular weight oligomer gelation reactions. In all the oligomer–polymer systems, however, the majority of the gelation, as indicated by the increases in  $G'$ , closely followed in time the uptake of the oligomers by the PAAm.

#### Modeling of the Oligomer–PAAm Uptake Data

A model of the oligomer–PAAm uptake could be used to predict both the uptake and gelation rates, because the gelation reaction closely followed the uptake of the oligomers by the PAAm. Assuming that the rates of oligomerization are small compared to the rates of oligomer–PAAm uptake, the gelling solution is assumed to contain only one

oligomer. The oligomer uptake is then described by eq. (1).<sup>8</sup>

$$\frac{d[Cr_i]}{dt} = \frac{-k_i(op)[Cr_i]^i[\text{PAAmcarboxyl}]^{m_i}}{fn([H^+])} \quad (1)$$

where  $Cr_i$  is the Cr oligomer with  $i$  Cr (III) atoms.

Previous studies indicate that the reaction between monomeric Cr(III) and the carboxyl group is approximately first order in Cr(III) and carboxyl, with an inverse  $[H^+]$  dependence.<sup>8</sup> Assuming that the first-order Cr(III) and carboxyl dependencies and inverse  $[H^+]$  dependencies apply to the oligomer–PAAm carboxyl reactions here, eq. (1) then becomes eq. (2).

$$\frac{d[Cr_i]}{dt} = \frac{-k_i(op)[Cr_i][\text{PAAmcarboxyl}]}{[H^+]} \quad (2)$$

Using the experimental conditions of relatively constant  $H^+$  and PAAmcarboxyl concentrations, a pseudorate constant,  $k'_i(op)$ , was defined with eq. (2) becoming eq. (3), whose solution is then eq. (4).

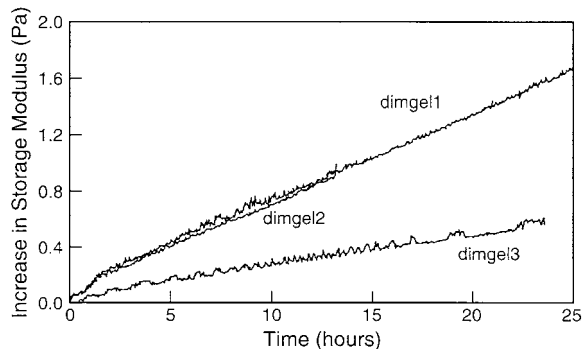
$$\frac{d[Cr_i]}{dt} = -k'_i(op)[Cr_i]$$

where

$$k'_i(op) = \frac{k_i(op)[\text{PAAmcarboxyl}]}{[H^+]} \quad (3)$$

$$\ln\left(\frac{[Cr_i(t)]}{[Cr_i(\text{total})]}\right) = -k'_i(op)t. \quad (4)$$

If this model, referred to here as the elementary reaction model with assumed low rates of oligomerization (ERLO), correctly describes the



**Figure 7** The effect of dimer concentration on the increase in  $G'$  for the gelation runs at pH 4 using 10.9 ppm Cr(III) (dimgel3) and 21 ppm (dimgel1 and dimgel2) (Table III).



**Table V** Effects of the Gelling Solution pH on the Rates of Gelation

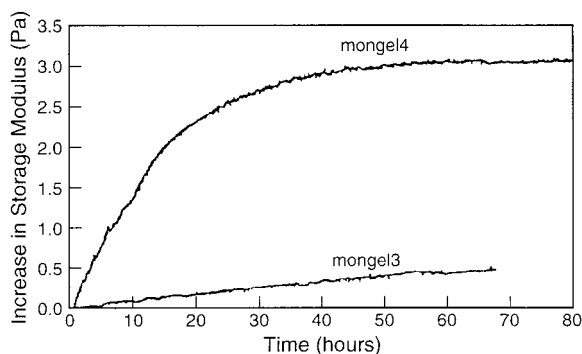
Gelation Run(s)	pH	Average [Cr(III)] (ppm)	Average Initial Slope (Pa/h)	Ratio, Slope <sub>pH5</sub> /Slope <sub>pH4</sub>	G' - G'' Crossing Time (h)
mongel3	4	11.7	0.008		no crossing
mongel4	5	11	0.19	24	15
dimgel3	4	10.9	0.024		no crossing
dimgel4	5	8.3	0.19	7.9	24
trigel3 and trigel4	4	7.4	0.295		10.6
trigel5	5	11	1.1	3.7	2.6

experimental uptake data, a plot of the  $\ln(Cr_i(t)/Cr_i(\text{total}))$  values vs. time would be linear with the slopes equal to  $k_i'(op)$ . In addition, the values of  $k_i'(op)[H^+]$  would be linear with PAAmcarboxyl concentration with slopes of  $k_i(op)$ .

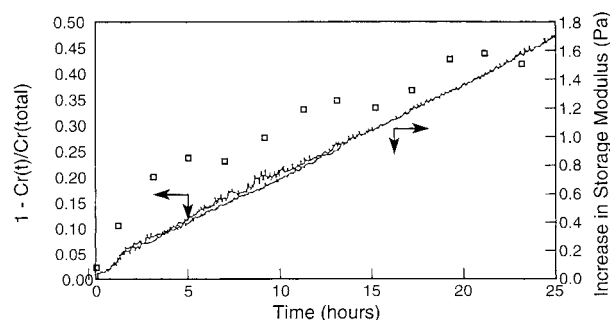
The model was first tested on the pH 4 monomer uptake data where relatively low rates of oligomerization were expected.<sup>8</sup> The first-order Cr(III) dependence was checked by performing regressions on the  $\ln([Cr(t)]/[Cr(\text{total})])$  values vs. time. The regressions were performed with JMP-IN, a SAS-equivalent Macintosh statistics software program. Good agreement was obtained between the regressed and experimental  $\ln([Cr(t)]/[Cr(\text{total})])$  values (Fig. 12) with relatively high goodness of fit values (0.94–0.96).<sup>8</sup> A linear regression was then performed on the experimental  $k_i'(op)[H^+]$  values vs. the PAAmcarboxyl concentrations, yielding a regression line slope ( $k_1(op)$ ) of  $1.07 \times 10^{-4} \text{ h}^{-1}$  with a goodness of fit of 0.944.<sup>8</sup> The combination of the good linear fits of the  $\ln([Cr(t)]/[Cr(\text{total})])$  values with time and the  $k_i'(op)[H^+]$  values with PAAmcarboxyl concentration indicated that the first-order

Cr(III), first-order PAAm dependencies found in other studies for the Cr(III)–carboxyl systems could be applied to the oligomer–PAAm systems here under the conditions where relatively low rates of oligomerization were expected.

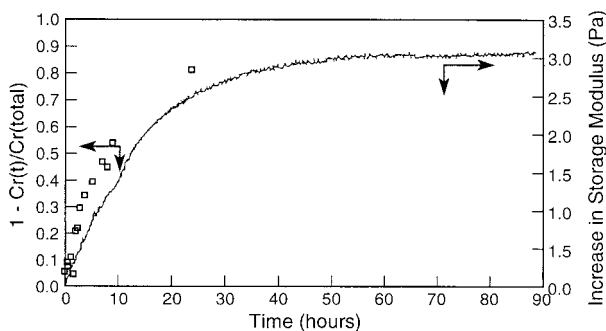
The results from the pH 4 monomer data were compared against the results obtained by Hunt,<sup>1</sup> who performed experiments using monomeric Cr(III) salts with PAAm in a 0.1M KNO<sub>3</sub> brine. Linear regressions were performed on the Cr(III) uptake data from the pH 4, 5000 ppm PAAm, 50 ppm Cr(III) system of Hunt where relatively small amounts of oligomerization were expected.<sup>8</sup> Regressions were performed with both the Cr(III) order obtained by Hunt (1.32) and the first-order Cr(III) order obtained here. The goodness of fit values were essentially identical (0.953–0.954), indicating that Cr(III) order was relatively insensitive over the Cr(III) uptake range used here for modeling. Assuming a first-order Cr(III) dependence and a linear [PAAm] dependence, a  $k_1(ol)$  value of  $1.43 \times 10^{-3} \text{ h}^{-1}$  was obtained for the Hunt data, approximately 13 times higher than the  $k_1(ol)$  of  $1.07 \times 10^{-4} \text{ h}^{-1}$  obtained here in 1M NaClO<sub>4</sub>. The higher rate con-



**Figure 8** The effect of pH on the increase in  $G'$  for the monomer gelation runs using 10.9–11.7 ppm Cr(III), 14,965–15,000 ppm PAAm, and pH values of 4 (mongel3) and 5 (mongel4) (Table III).



**Figure 9** Comparison of the fractional uptake and the increase in  $G'$  for the pH 4, 21–24.3 dimer, 14,415–14,879 ppm PAAm uptake and gelation runs (dimupt2, Table I; dimgel1, dimgel2, Table III).

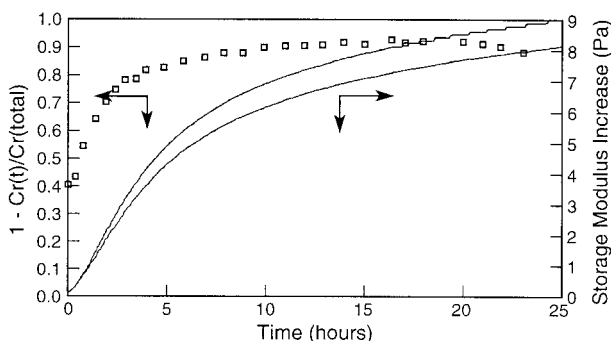


**Figure 10** Comparison of the fractional uptake and increase in  $G'$  for the pH 5, 10.9 ppm monomer, 15,000 ppm PAAm uptake and gelation run (monupt5, Table I; mongel4, Table III).

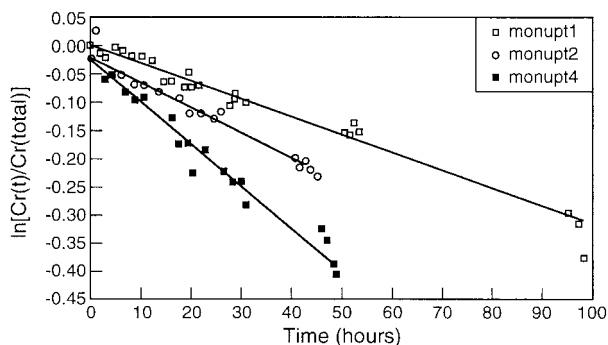
stant obtained with the Hunt data indicates that the uptake reaction was significantly faster in the Hunt 0.1M  $KNO_3$  brine as compared to the reaction in 1M  $NaClO_4$  brine.

The ERLO model was also applied to the dimer and trimer pH 4 runs where several different PAAm concentrations were used. Both sets of data showed model deviations from the experimental data, with deviations occurring primarily in the initial time periods for the dimer runs and for both the initial and late reaction time periods for the trimer runs.<sup>8</sup>

There are several possible explanations for the lack of model fits to the dimer and trimer data including the occurrence of significant oligomerization during the uptake reaction, rapid initial oligomer uptake during gel solution preparation, a difference in reactivity between oligomers and oligomer products, mass transfer limitations due to increases in the gelling solution viscosity, and residual free-solution oligomer concentration at



**Figure 11** Comparison of the fractional uptake and increase in  $G'$  for the pH 4, 19–22.8 ppm trimer, 13,153–14,980 ppm PAAm uptake and gelation runs (triupt3, Table I; trigel1, trigel2, Table III).



**Figure 12** Plots of the experimental and ERLO-model  $\ln[Cr(t)/Cr(total)]$  values for the pH 4 monomer uptake runs at different PAAm concentrations (see Table I for descriptions of the experimental conditions for the individual runs).

equilibrium. These possibilities are explored in more depth by Dona.<sup>8</sup>

## SUMMARY AND CONCLUSIONS

The uptake and gelation reactions of Cr(III) monomer, dimer, and trimer with partially hydrolyzed (2.3% carboxyl groups) PAAm were investigated. The rates of the uptake and gelation reactions increased with increasing oligomer size, oligomer concentration, and solution pH. The gelation reactions, as indicated by the gelation times and the increases in the gelling solution  $G'$  values, closely followed in time the uptake of oligomers by the PAAm.

In the pH 4 monomer uptake runs, where relatively low ratios of oligomerization-to-uptake rates occurred, a good fit to the data was obtained using an uptake model that was based on the assumptions of elementary reactions and low oligomerization rates (the ERLO model). The ERLO model did not, however, fit the dimer or the trimer data in a satisfactory manner.

## NOMENCLATURE

$Cr(t)$  = amount of free chromium in the system at time  $t$

$Cr(total)$  = total amount of chromium in the system

$G'$  = storage modulus

$G''$  = loss modulus

$k_i(op)$  = uptake rate constant of the reaction of the primary oligomer with PAAm-

- carboxyl ( $\text{h}^{-1}$ )  
 $k'_i(\text{op}) =$  pseudofirst-order uptake rate constant for the reaction of the primary oligomer with PAAmcarboxyl =  $k_i(\text{op}) \times [\text{PAAmcarboxyl}]/[\text{H}^+]$   
 $l_i =$  Cr(III) rate order for the uptake of the primary oligomer with PAAmcarboxyl  
 $m_i =$  PAAmcarboxyl rate order for the uptake of the primary oligomer with PAAmcarboxyl  
 $t =$  time  
 $fn[ ] =$  function of concentration of indicated species  
 $[ ] =$  concentration of indicated species

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